Solar High-Temperature Water Splitting Cycle with Quantum Boost

P.I.: Robin Taylor
Presenter: Lloyd Brown
Science Applications International Corp.
San Diego, California

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PD027

Overview

Timeline

- Start Date: 09/01/2007
- End Date: 10/31/2013
- Percent Complete: 85%

Budget

- Total project funding
  - DOE share: $3.7M
  - Contractor share: $910k
- Funding recvd. in FY12: $700k
- Funding for FY13: $600k

Barriers

U. High-Temperature Thermochemical Technology
V. High-Temperature Robust Materials
W. Concentrated Solar Energy Capital Cost
X. Coupling Concentrated Solar Energy & Thermochemical Cycles
- DOE Threshold Cost Goal: $2-4/kg
- STH Energy Conversion Goal: 26%

Partners

- SAIC (Lead)
  Solar System/Receiver

- UCSD/TChemE
  Thermochemical Process

- Electrosynthesis
  Salt Electrolysis

- Southern California Gas Company
  Utility Interface

Overall Project Objectives

- RD&D of the Viability of a <u>New</u> & Improved Sulfur Family Thermochemical Water-Splitting Cycle for large-scale hydrogen production using <u>solar</u> energy
- More Specifically, Overall Project Goals are to:

  Evaluate sulfur ammonia (SA) water-splitting cycles that employ photocatalytic (quantum boost[1]) or electrolytic hydrogen evolution steps and perform lab testing to demonstrate feasibility of the chemistry
    - Perform economic analyses of SA cycles as they evolve
    - Select a cycle that has high potential for meeting the DOE threshold cost goal of $2-4/kg solar to hydrogen energy conversion goal of 26%
    - Demonstrate technical feasibility of the selected SA cycle in bench-scale, closed-loop tests
    - Demonstrate pre-commercial feasibility by testing and evaluating a fully-integrated pilot-scale closed-cycle solar hydrogen production plant

Past Year Project Objectives

- Continue Optimization of Electrolytic Oxidation Process
    - Continue development of better catalysts that lower the over-potential at the anode & allow operation at high current densities
    - Maintain pH at anode and cathode to avoid formation of reduced sulfur species
    - Perform 500 hour durability test & cell design improvement
    - Electrochemical cell design optimization and scale-up
- Complete Evaluation of High-Temperature K_2SO_4 Sub-Cycle
- Economic and Solar System Analysis
    - Continued Refinement of the Solar Field, Aspen Plus®, and H2A Analyses
    - Evaluation of storage for 24/7 operation of the total chemical plant, thermal management strategies and receiver materials

  1 - Quantum Boost: The use of high energy photonic (quantum) portion of sunlight for photocatalytic production of hydrogen and the remaining thermal portion of sunlight for oxygen production.

Impact on Program Barriers

- **U. High-Temperature Thermochemical Technology** – This project is developing a new thermochemical cycle intended to operate at lower temperatures and be more cost effective than other cycles.

- **V. High-Temperature Robust Materials** – Materials able to operate in the high temperatures and caustic environment of the receivers and reactors are being developed.

- **W. Concentrated Solar Energy Capital Cost** –System costs are being reduced by optimizing the solar-chemical plant interface.

- **X. Coupling Concentrated Solar Energy & Thermochemical Cycles** – The solar field and receivers are being evaluated and designed to provide appropriate amounts of energy at necessary temperature levels and with appropriate controls.

Approach

- Develop an Improved Sulfur-family Thermochemical Water-Splitting Cycle

- Conduct Laboratory Evaluation of all Processes within the Cycle

- Develop Comprehensive Aspen Plus® Modeling of the Cycle and Modifications

- Perform H2A Analysis of the Modeled Cycle(s) to Compare Design and Operational Approaches

- Design a Solar Collector Field and Receivers to Complement Chemical Process and Maximize Solar/System Efficiency

- Refine Process with Improvements Suggested by Lab Testing, Solar Configuration Studies, and H2A/Aspen Plus® Analyses

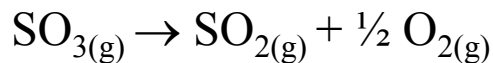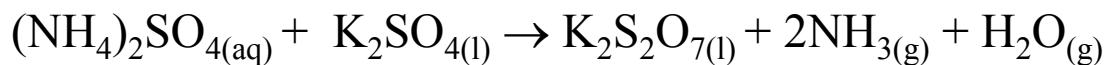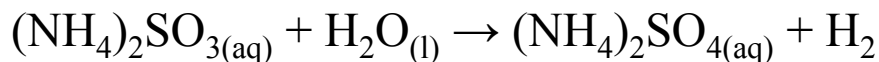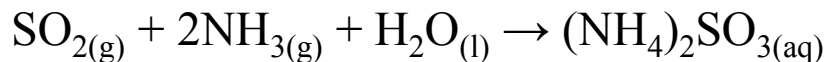- Perform Bench-Scale Testing of Individual Chemical Processes, then Integrated Pilot-Scale Testing

Previous Years' Milestones

Mo./Year % Comp.	Milestone or Go/No-Go Decision	Status
Sep 2008 100%	Select a photo/thermo-chemical water splitting cycle that uses photonic portion of solar spectrum for H_2 production and thermal portion for O_2 production.	Photocatalytic sulfur ammonia cycle selected with $ZnSO_4$ O_2 production.
May 2009 100%	Improve photocatalytic performance. Identify cost effective solar heliostat designs.	Photocatalyst efficiency improved 12% to 28% with CdS. Demonstrated ½ scale low cost GRC solar heliostat. H2A shows photocatalytic cycle won't meet DOE cost goals.
Sep 2010 100%	Prove electrolytic H_2 sub-cycle, all liquid pyrosulfate/sulfate O_2 sub-cycle and solar concentrating system are viable.	H_2 and O_2 sub-cycles and compatible solar concentrating system proven viable.
Aug 2011 100%	Demonstrate electrochemical cell with voltage < 0.8V at current density >50 mA/cm^2, show cycle can be closed.	Cell operated at 0.8V, 150 mA/cm^2 at 130°C, cycle closed.
Feb 2012 100%	Reduce cell voltage < 0.64V at >50 mA/cm^2. Prove molten salt will flow and NH_3 evolves separate from SO_3.	Cell operated at 0.64V at 50 mA/cm^2 at 127°C. Molten salt will flow. NH_3 & SO_3 evolve separately.
Aug 2012 100%	Operate electrochemical cell 500 hours at optimal conditions from 2012 milestone.	500 hour test ran successfully at 1.1V, 100 mA/cm^2 at 100°C with no voltage degradation but at higher than optimal voltage.

Current Year Milestones

| Mo./Year % Comp.	Milestone or Go/No-Go Decision	Status
Sep 2013 40%	Improve electrolytic H_2 production by developing better anode electrocatalysts to facilitate operation at lower temperatures (80 ^{o}C) while maintaining low voltage (< 0.8V) and/or identifying alternate membranes that can operate at higher temperature without an unacceptably high flux of sulfite across the membrane (<0.1 mmole/m^2/s).	New developmental membranes show significant improvement. This may allow significant decrease in cell voltage and higher temperature operation.
Sep 2013 40%	Use Aspen Plus$^®$ modeling tool to optimize systems for input to the H2A economic model. Evaluate using heat from excess electricity production for SO_3 decomposition. Evaluate power recovery and electrical power generation alternatives.	Plant operation has been lowered to 800°C; includes 24/7 operation with phase change energy storage. Rankine power cycles efficiently generate electricity with excess heat. Need additional optimization.
Sep 2013 40%	Perform technical and economic analyses of SA cycle systems with and without a high temperature storage system that would allow for 24/7 operation.	Costs have been updated with H2Av3 and now include 24/7 operation. More optimization is needed.

SA Process with 24/7 Chemical Plant Operation

$$SO_{2(g)} + 2NH_{3(g)} + H_2O_{(l)} \rightarrow (NH_4)_2SO_{3(aq)}$$

$$(NH_4)_2SO_{3(aq)} + H_2O_{(l)} \rightarrow (NH_4)_2SO_{4(aq)} + H_2$$

$$(NH_4)_2SO_{4(aq)} + K_2SO_{4(l)} \rightarrow K_2S_2O_{7(l)} + 2NH_{3(g)} + H_2O_{(g)}$$

$$K_2S_2O_{7(l)} \rightarrow K_2SO_{4(l)} + SO_{3(g)}$$

$$SO_{3(g)} \rightarrow SO_{2(g)} + \tfrac{1}{2}\,O_{2(g)}$$
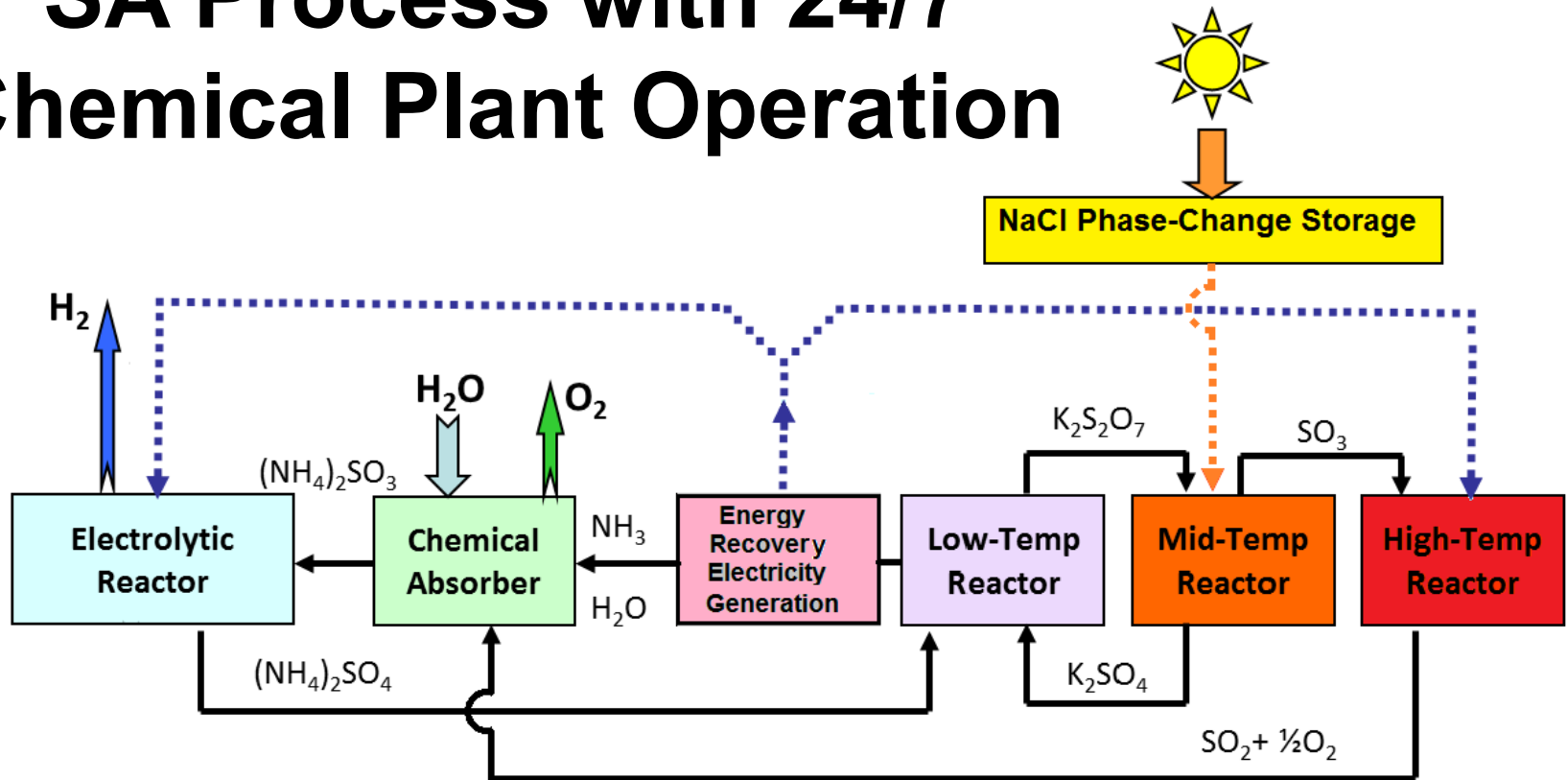
1. chem. absorption 25-50°C
2. electrolytic   80-150°C
3. adiabatic mixing 400-450°C
4. stored thermal   790°C
5. electric   850-1,200°C

8

High-Temperature Phase-Change Storage System

- Storage needed to achieve 24/7 operation of the chemical plant
- The mid-temperature reactor requires ~800°C
- NaCl phase-change storage with direct-contact sodium liquid metal heat-pipe energy delivery can meet these requirements
  - Provides large heat capacity at ~800°C (481 kJ/kg)
  - Simple interface and high conductivity for delivery of heat to/from storage
  - Pressures are near-atmospheric
  - Low-cost storage medium
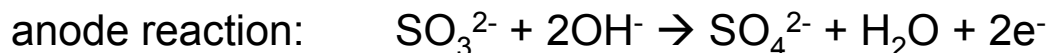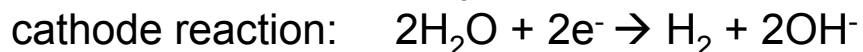 - Concept has been demonstrated by others at lab scale
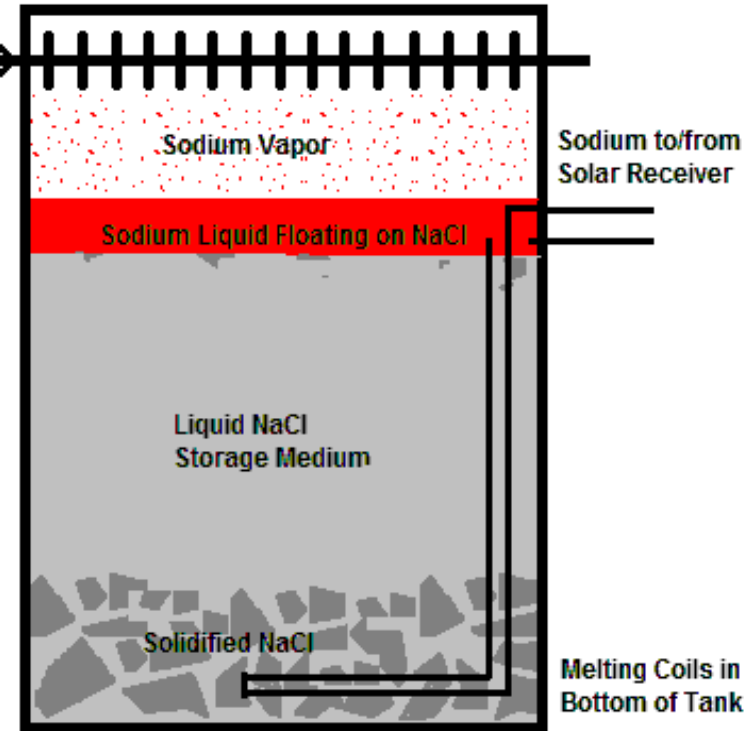
Reference: J. Phys. IV France v.9 Pr3-89 (1999), "High temperature thermal energy storage an experimental study," Adinberg, R., Yogev, A., and Kaftori, D.

Molten Salt to be Heated

Sodium Vapor

Sodium to/from Solar Receiver

Sodium Liquid Floating on NaCl

Liquid NaCl Storage Medium

Solidified NaCl

Melting Coils in Bottom of Tank

Electrolysis Progress: Reduced Overpotential with Improved Membranes and Electrocatalysts

In basic media

anode reaction: $SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-$ $E^o = -0.936$ V

cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^o = -0.828$ V
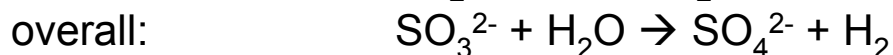
overall: $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + H_2$ $E^o_{cell} = -0.108$ V

- In basic media, the thermodynamic potential required to drive this reaction is very small. In practice, there is an overpotential required to overcome the kinetics of the reaction. We have determined that the anode reaction is the main source of overpotential in the cell. In order to address this we have evaluated a wide range electrocatalysts and operated at elevated temperature

- New catalysts and electrode materials have been tested over a range of current densities and temperatures (80 – 130°C). Promising materials include spinels $M_xN_{3-x}O_4$ (where M,N=Fe/Ni/Co), Pt/Co, cobalt and vanadium oxides. Catalysts have included nano-materials.

- Quantitative hydrogen production with efficient sulfite oxidation has been verified with divided cells.

Approximate Contributions to Overall Cell Voltage
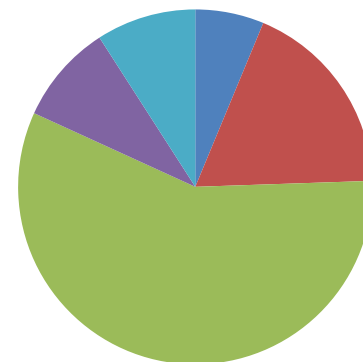
- ■ Thermodynamic Voltage, at 50% conversion
- ■ Membrane, FX 7050
- ■ Anode Overpotential
- ■ Cathode Overpotential

10

Electrolysis Progress: High Temperature and Pressure Required to Reach Voltage Targets

- Concluded that we need to operate at high temperature to reach voltage targets.
- High temperatures require operation at high pressure.
- Pressure reactor capable of 150 psi and 130°C.
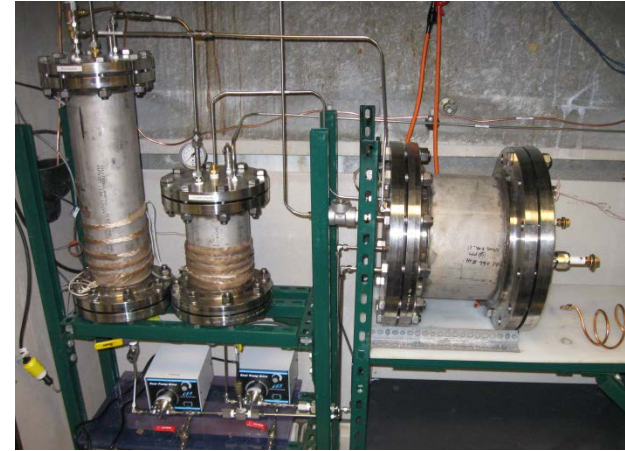
813-74/75,77, 125-127°C and 80psi
1/2 Pt/Co felt anode / NR112, 195ugPt/cm²

— 125 °C, 0% Conversion
— 127 °C, 50% Conversion
— 127 °C, 90% Conversion
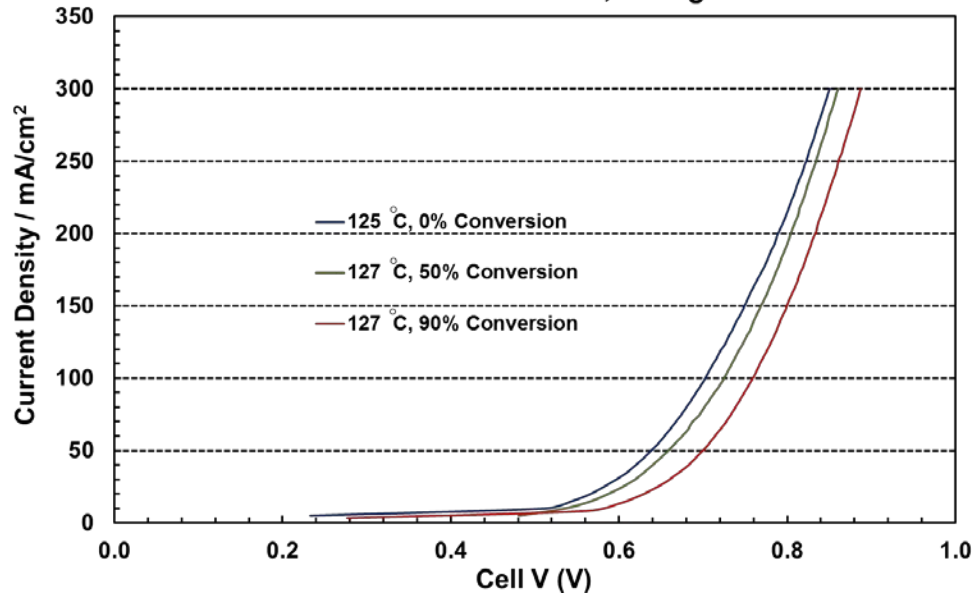
Thermodynamic calculations predict that we should see a voltage increase of about 70 mV during a batch electrolysis. Additional voltage changes could be seen as a result of pH variations. Current potential curves using synthetic solutions confirm these predictions. Therefore, long term stability measurements of cell voltage should only be compared _at the same electrolyte conditions._
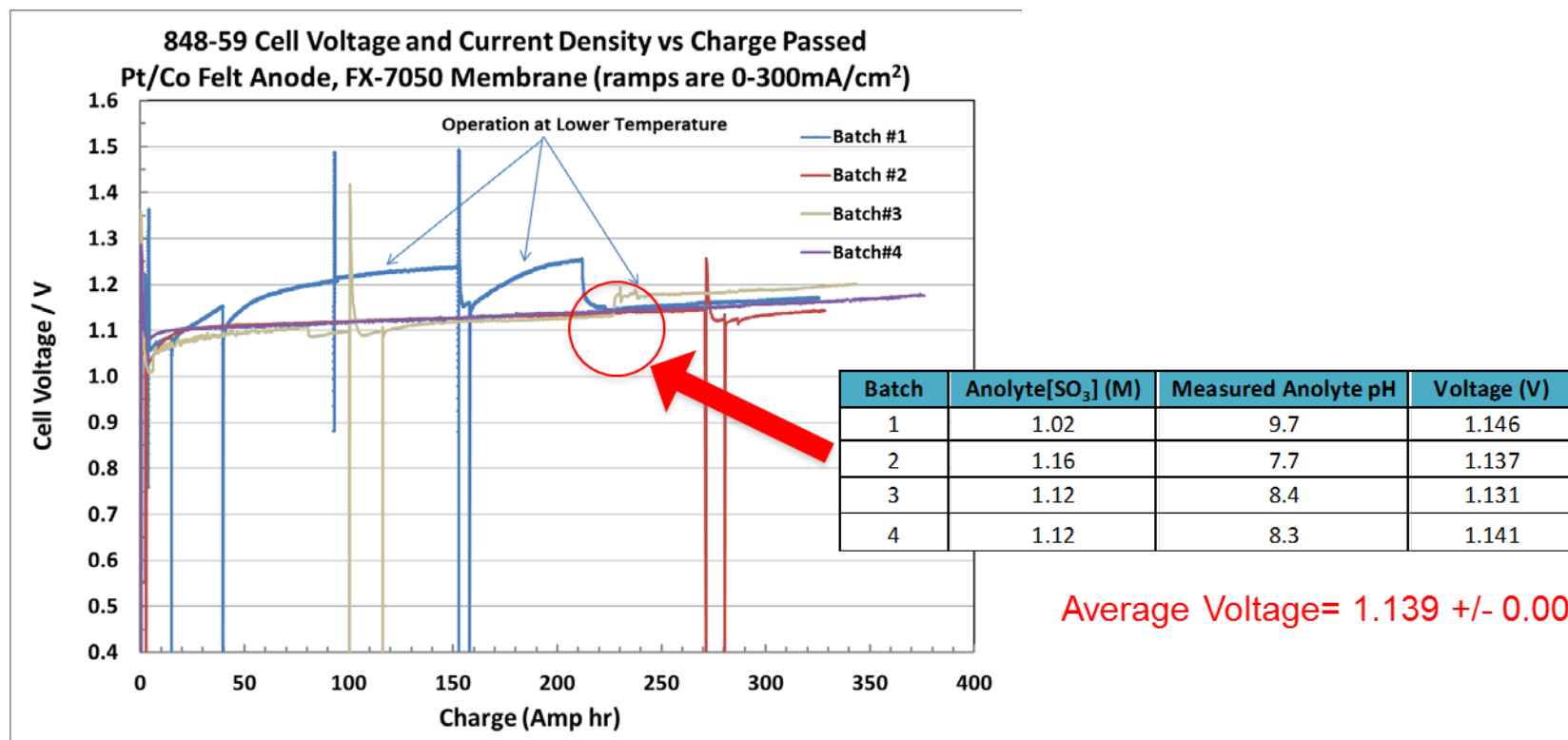
11

Electrolysis Progress

Summary of Long Term Test Data	
Total Electrolysis Time	550 hours
Cell Voltage at 100 mA/cm^2 over a batch.	1.09 - 1.17 V
Hydrogen Efficiency	94% (Faradaic)
Sulfite Flux averaged over 550 hours	1.7×10^{-4} mole/m^2/s
Water Transfer across membrane	3.1 mole H_2O/mole of charge passed

848-59 Sulfite Concentration vs Charge Passed
Pt/Co Felt Anode, FX-7050
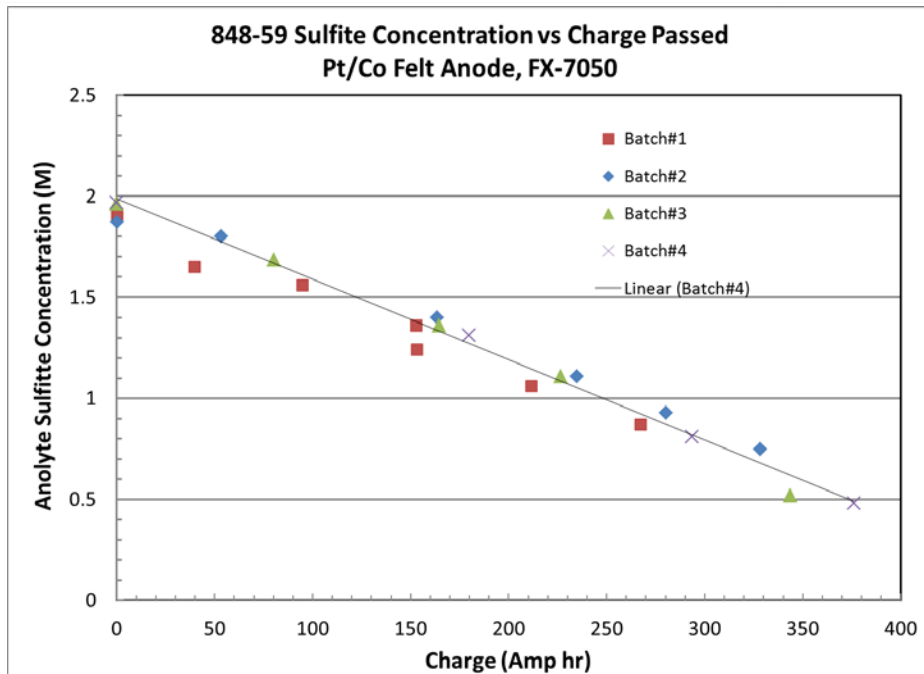
- Long-term performance was evaluated over a 550 hour test. This was conducted in four consecutive batch electrolysis runs each showing the same performance.
- Anolyte was initially 2M ammonium sulfite, running at 100 ^{o}C.
- Better membranes are required to run at higher temperature due to sulfite flux. Membrane used for this test had higher resistance but lower sulfite flux.

12

Electrolysis Progress

848-59 Cell Voltage and Current Density vs Charge Passed
Pt/Co Felt Anode, FX-7050 Membrane (ramps are 0-300mA/cm^2)

Batch	Anolyte[SO$_3$] (M)	Measured Anolyte pH	Voltage (V)
1	1.02	9.7	1.146
2	1.16	7.7	1.137
3	1.12	8.4	1.131
4	1.12	8.3	1.141

Average Voltage= 1.139 +/- 0.006V

- Cell Voltage shown as a function of charge passed for four consecutive batch electrolyses; note that the cell voltage increases with conversion as predicted.
- Electrolysis ran for 550 hours with a stable and **reproducible voltage (+/- 0.5%)** at the same electrolyte conditions.

13

Improvements in Electrolysis

- It should be possible to further reduce the cell voltage by running at higher temperatures. This requires significant membrane improvements over those used in the long term testing; specifically a reduction in the sulfite transport.
- Sulfite transport across the membrane leads to unwanted cathode reactions and a reduction in hydrogen efficiency.
- A range of membrane materials have been evaluated and sulfite flux measurements made.
- We have identified membranes with up to 2 orders of magnitude lower sulfite fluxes even after treatment at 140 °C

| Membrane and Pre-conditioning	Sulfite Flux $\mu mol/m^2/sec$
Nafion®NR212 (Initial Low Resistance Membrane)	
As Received	18
Soaked at 120^0C and 85psi for 3 days	970
FX7050, (Membrane used in 500 Hour Test)	
Boiled DI water 0.5hr	250
Soaked 1200C, 85psi for 3.5days	190
DuPont® Developmental Membrane	
As received	1.3
Soaked 120^0C, 80psi for 7.75 days and then 140^0C, 90psi for 4.9days	2.6

Summary – Oxygen Sub-cycle

- The experiments confirmed the viability of the oxygen sub-cycle.
  - NH_3 and SO_3 can be evolved separately.
  - Lower melting temperatures were achieved with a combination of Na- salts and K- salts.
  - Molten salts have low enough viscosity to be pumped.
  - Decomposition of SO_3 is proven technology thus laboratory demonstration was not necessary.

Reference: Wang, M, "Study of the Thermochemistry for Oxygen Production for a Solar Sulfur-Ammonia Water-Splitting Process," MS thesis, University of California, San Diego (2012).

Aspen Plus® Process Model

- 24/7 production of hydrogen
  - Thermal storage system heats Mid-T reactor
  - Low-T reactor is adiabatic
- 9 bar operating pressure set for maximum efficiency at electrolyzer temperature
- Overall efficiency 20%+

- Rankine-cycle power plants
- Recover energy from SO_2 and NH_3 streams and excess heat from electrolyzer
- Generate electricity to power the electrolyzer and heat the High-T reactor
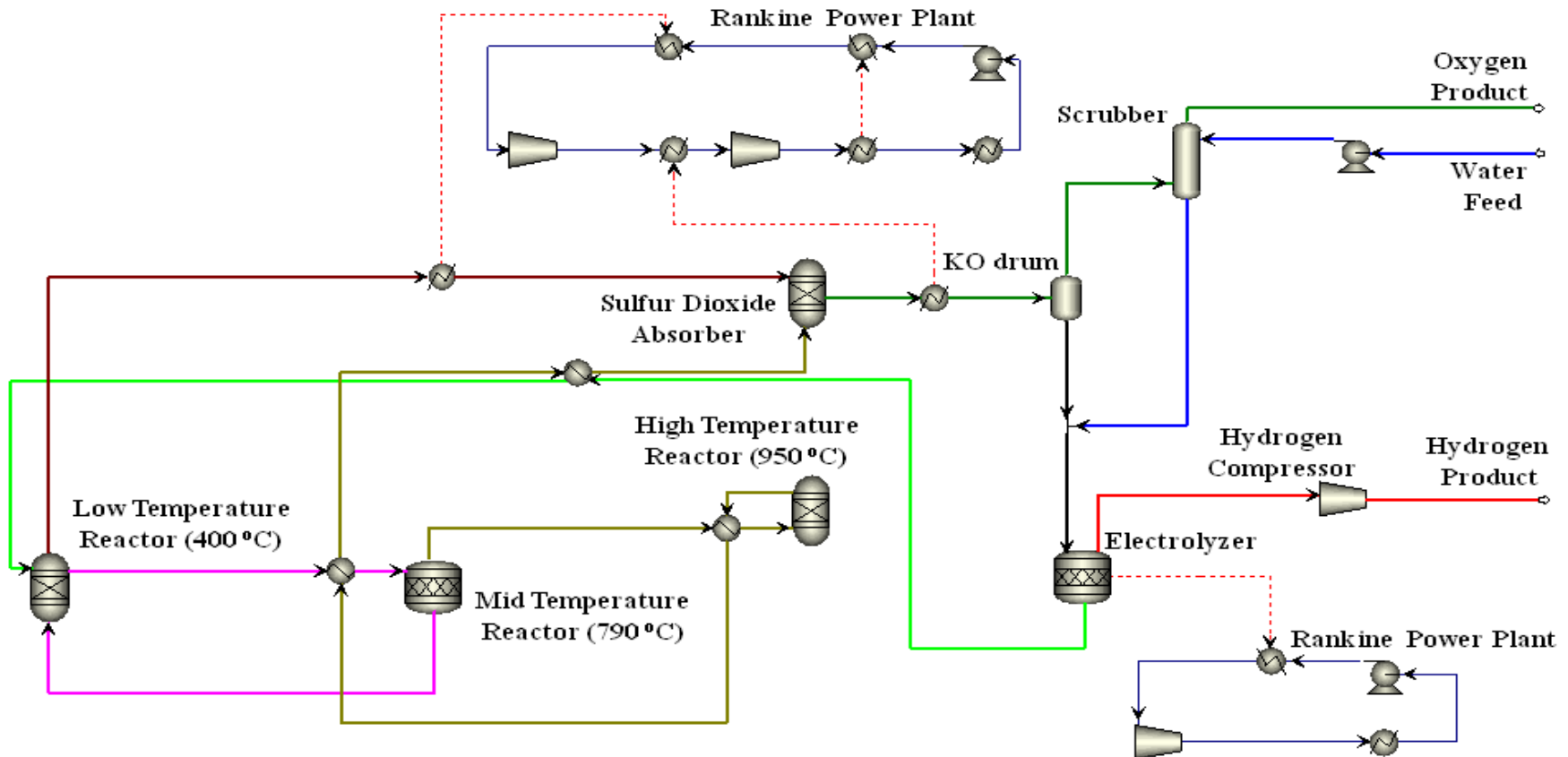
Aspen Plus® Process Model Improvements

- **Mid temperature reactor:**
  - Reactor temperature was lowered to 790°C by varying molten salt composition to accommodate a phase-change thermal-storage system with NaCl for continuous plant operation
- **Power recovery system:**
  - Rankine power cycles were designed to recover excess heat to generate electricity
  - Design specifications were implemented to prevent temperature crossovers in heat exchangers, thus making the power recovery systems more practical
  - Sensitivity blocks were also incorporated to plot temperature profiles of cooling and heating streams to verify design specifications
- **Optimization:**
  - Overall plant pressure was varied to study the effects of plant pressure on plant efficiency and power recovery

Solar System Heat Collection Module

- Central Receiver with North-Field Layout, Cavity Receiver, and Phase-Change NaCl Storage
- Sized to deliver a nominal 50 MW$_{th}$ to chemical plant*
- 231,600 m^2 Heliostats
- 150 m Tower Height
- ~800°C Delivery Temperature to Process
- Performance (Barstow, CA)
    - 150 MW$_{th}$ peak power
    - 1196 MWh$_{th}$ peak daily delivery
      (= 50 MW averaged over 24 hrs)
    - 32.3 MW$_{th}$ average over year
    - 44% average efficiency,
      solar to thermal energy
      (includes weather, thermal,
      & optical losses)
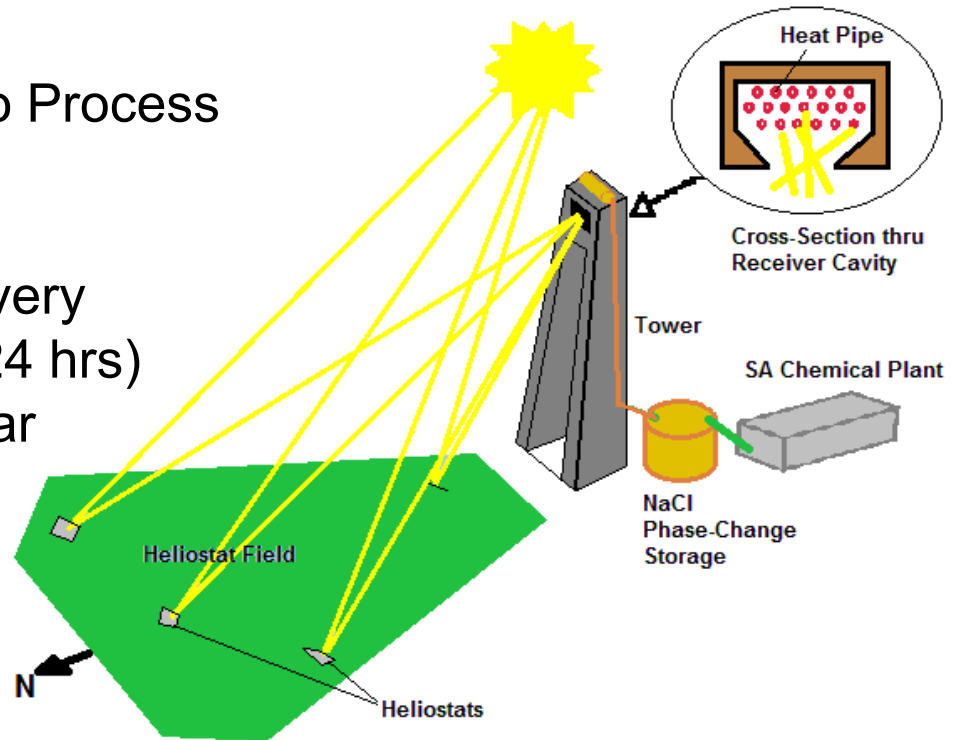
* Results from NREL Solar Advisor Model (SAM)

H2A Hydrogen Production Cost Results

- **Implemented Analysis in H2A Version 3**
- **50 MW$_{th}$ Modular Plant Design**
  - $55 million Solar Plant Module Cost (with storage)
  - $17 million Process Plant Cost (including Electrolytic Plant)
  - ~5,000 kg/day Average Hydrogen Plant Production
  - 2015 Hydrogen Production Cost:
    - Capital $ 9.77   82.0%
    - Fixed O&M $ 2.07   17.5%
    - Other $ 0.05   0.5%
                            Total: **$11.89/kg Hydrogen**
  - **2020 Estimate: $7.67/kg**
    - Includes process and solar plant improvements
- **20 Plants Required to Produce 100,000 kg/day ($1,440 M)**

Project Partners & Key Personnel

Science Applications International Corp. (SAIC)– Prime (Industry)
- Key Personnel: Rob Taylor, Roger Davenport
- Project management & system integration
- Solar concentrator/receiver evaluation & design
- Thermal reactor optimization & design
- Economic evaluation & hydrogen production cost estimates

University of California, San Diego (UCSD) – Sub (Academia)
- Key Personnel: Jan Talbot, Richard Herz (3 Graduate & 2 Undergraduate Students)
- Laboratory testing & thermochemical cycle development
- Chemical plant analysis

Thermochemical Engineering Solutions (TChemE) - Sub (Industry)
- Key Personnel: Lloyd Brown
- Thermochemical cycle evaluation & analysis

Electrosynthesis Company, Inc. – Subcontractor (Industry)
- Key Personnel: David Genders, Peter Symons
- Electrolytic cell development & optimization

Southern California Gas Company – Team Member (Industry)
- Key Personnel: Kate Zeng, Jeff Reed
- End user/utility interface, cost sharing team member

20

FY13/FY14 Activities

- **Continue Optimization of Electrolytic Process**
  - Catalyst development
    - Lower anode over-potential at high current densities
    - Increase effective surface area (nanoparticles).
    - Increase cathode hydrogen selectivity in presence of sulfite
  - Alternate membrane screening
    - High temperature operation with low sulfite flux

- **Chemical Plant Modeling and Solar System Analysis**
  - Aspen Plus® flowsheet optimization
    - Maximize hydrogen production efficiency
    - Trade-off studies of power recovery options
    - Provide input to the H2Av3 economic model
  - Develop 24/7 chemical plant option
    - Use excess electrical generation capability to decompose SO_3
    - Incorporate high temperature phase change thermal storage system

- **Economic Analysis**
  - Improve cost estimates quality through initial design of key process equipment
  - Update H2Av3 Economic Analyses using latest information

Summary

- **Electrolytic Step Accomplishments**
  - Long term stability of complete electrochemical system demonstrated (500+ hour extended run)
  - New membranes identified with up to 2 orders of magnitude lower sulfite fluxes

- **All-Fluid High-Temperature Oxygen Generation Step**
  - Laboratory resolution of potential show stoppers
    - Separation of NH_4 and SO_3 demonstrated using sulfate/pyrosulfate molten salt system
    - Increased molten salt liquid range demonstrated
    - Low molten salt viscosity measured
  - Entire process consists of elementary chemical engineering unit operations, all in widespread industrial use for over 100 years

- **Aspen Plus® used to model significant process improvements**
  - Phase-change thermal-storage system with NaCl incorporated allowing 24/7 continuous plant operation
  - Rankine power cycles were designed to recover excess heat and efficiently generate electricity
  - Overall plant pressure and SO_3 decomposer temperature were varied to optimize plant efficiency and power recovery

- **Solar Configuration Focus is 50 MW$_{th}$ Central Receiver System with NaCl Molten Salt Storage to Allow 24/7 Operation and produce 5,000 kg/day H$_2$ per module**

- **H2A version 3 was used to optimize and trade-off SA cycle configurations**

- **Conclusion:**
  - The Sulfur-Ammonia cycle is unique in that it is an all fluid cycle (no solids handling)
  - Relatively low temperature plant, solar receiver operates at 800ºC
  - Generates all electricity needed internally
  - Operates 24/7 with low cost storage
  - Good potential STCH cycle for reaching DOE cost goals

Technical Back-Up Slides

Detailed Past Milestones (1 of 2)

Mo./Year % Comp.	Milestone or Go/No-Go Decision	Status
Sep 2008 100%	Select a photo/thermo-chemical water splitting cycle that uses thermal portion of solar spectrum for O_2 production and high energy photonic part for H_2 generation. Develop Aspen Plus® model and evaluate preferred solar system configuration.	Photocatalytic sulfur ammonia cycle selected with $ZnSO_4$ O_2 production subcycle. Aspen Plus® model developed. Identified solar heliostat field design.
May 2009 100%	Improve photocatalytic performance. Identify cost effective solar heliostat designs. Evaluate cost of H_2 production with H2A economic model.	Photocatalyst optimization improved photon-to-H_2 energy efficiency from 12% to 28% with CdS doped with multi-metal catalysts. Demonstrated ½ scale low cost glass reinforced concrete (GRC) solar heliostat. H2A reveals photocatalytic process will not meet cost goals.
Sep 2010 100%	Prove electrolytic H_2 production sub-cycle is technically and economically viable. Prove all liquid pyrosulfate/sulfate O_2 sub-cycle is viable. Confirm viability of solar concentrating system.	H_2 and O_2 sub-cycles and compatible solar concentrating system proven viable.

Detailed Past Milestones (2 of 2)

| Mo./Year % Comp.	Milestone or Go/No-Go Decision	Status
Aug 2011 100%	Prove electrolytic H_2 production sub-cycle and overall sulfur ammonia cycle are technically and economically viable by demonstrating electrochemical cell with voltage < 0.8V at current density >50 mA/cm^2, and thermodynamic and chemical plant analyses show cycle can be closed.	Electrolytic cell operated at 0.8V, 150 mA/cm^2 at 130°C, Performed thermodynamic evaluation and cycle closed.
Feb 2012 100%	Reduce energy consumption of electrolytic H_2 sub-cycle 20% to achieve cell voltage < 0.64V at current density >50 mA/cm^2. Demonstrate viability of O_2 sub-cycle by proving the molten salt will flow and the NH_3 can be separated from the SO_3 with less than 10% recycle of SO_3 back to the electrolysis system.	Electrolytic cell operated at 0.64V at 50 mA/cm^2 at 127°C. Pyrosulfate/sulfate molten salt will flow and NH_3 can be separated from SO_3 with less than 10% recycle of SO_3 back to electrolysis system.
Aug 2012 100%	Prove electrolytic H_2 production sub-cycle and O_2 production sub-cycle are technically and economically viable by operating electrochemical cell 500 hours at optimal conditions from 2012 milestone, demonstrate viability of O_2 sub-cycle by defining conditions to separate SO_3 from the pyrosulfate/sulfate molten salt.	500 hour test ran below optimal at 1.1V, 100 mA/cm^2 at 100°C. No voltage degradation over testing period. Defined conditions to separate the SO_3 from the pyrosulfate/sulfate molten salt at 1 atm. Aspen Plus$^®$ model fully functional.

Advantages of the SA Cycle

- Solar SA cycle is a renewable & sustainable hydrogen production process
- Solar only cycle with no electricity imports, generates all electricity needed internally
- SA cycle is an all fluid (gas/liquid) cycle (no solid particles)
- SA cycle can operate at medium temperature (800°C) when using electric SO_3 decomposer thus avoiding high temperature materials problems
- There is only simple gas/liquid separation
- SA cycle has a high thermodynamic efficiency
- While the SA cycle appears to be complex it consists of only 3 chemical reactions plus absorbers, scrubbers and heat exchangers
- Entire process consists of elementary chemical engineering unit operations, all have been in widespread industrial use for over 100 years.
- All of the processes in the SA cycle have now been proven in the laboratory or have been fully demonstrated by others but needs to be optimized
- Team assembled is highly qualified and includes industry researchers, academia and an industry end user

Summary of SA Cycle Status

- Independent thermodynamic and chemical plant analyses show the cycle can be closed and indicates cycle viability

- Improvements to electrocatalysts and high temperature operation have achieved cell voltages as low as 0.64 V at 50 mA/cm^2 and 0.85 V at 300 mA/cm^2

- Completed 500 hour test at just over 1.1V, 100 mA/cm^2 at 100°C. Stable voltage observed over the entire test. The 500 hour test was not able to run at the optimal operating conditions. This will be addressed in Phase 2.

- Membranes have been identified with up to 2 orders of magnitude lower sulfite fluxes even after treatment at 140°C

- Lab results continue to prove the feasibility of the all-(liquid/gas) molten salt mixture of $(NH_4)_2SO_4$+ K_2SO_4+ $K_2S_2O_7$+ Na_2SO_4+ $Na_2S_2O_7$ chemistry for the high-temperature oxygen evolution sub-cycle.

- A thermochemical reactor with Residual Gas Analysis (RGA) equipment was used to show ammonia and sulfur trioxide can be evolved separately with a 25 – 50°C temperature difference.

- The melting points, densities and viscosities of the molten salt mixtures were measured and proved that the salt mixtures can be easily pumped.

- Sulfur trioxide decomposition has been adequately demonstrated many times over the past 30 years.

- The Aspen Plus$^®$ SA process modeling has been significantly improved and is now a robust fully functioning process tool.

- The Aspen Plus $^®$ model and the H2A economic model were used to optimize and trade-off SA cycle configurations

- Solar configuration evaluations were performed with the focus remaining on a central receiver system with molten salt storage to allow 24/7 operation.

Effect of pH on Anode Overpotential/ Cell Voltage

Potential for Sulfite Oxidation on Graphite in Various Solutions.
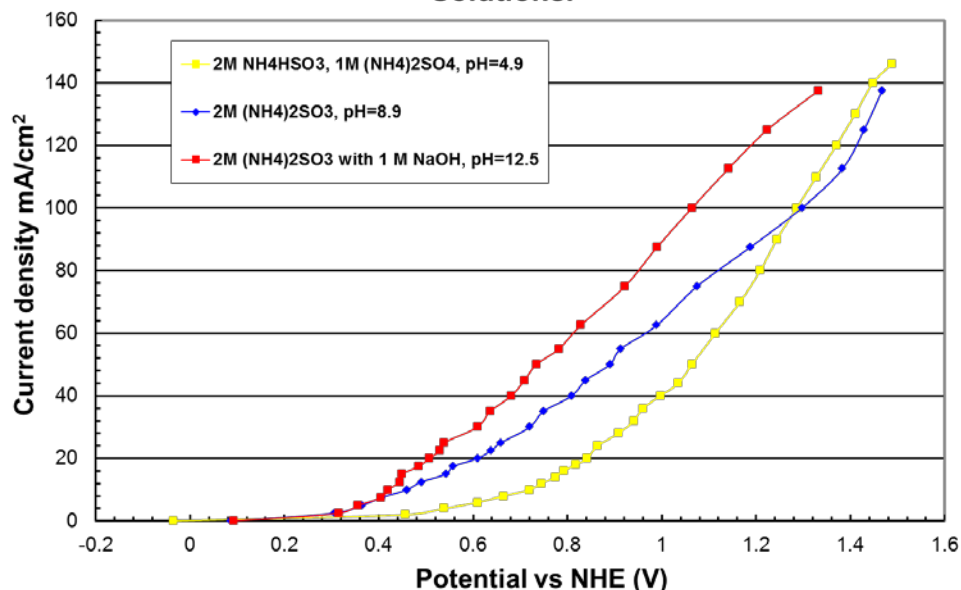
- Oxidation is kinetically slow. Potential needed to drive current is much higher than thermodynamic potential (more than 1 V overpotential).

- Anodic oxidation of sulfite and the cathodic hydrogen evolution reaction are pH dependent.
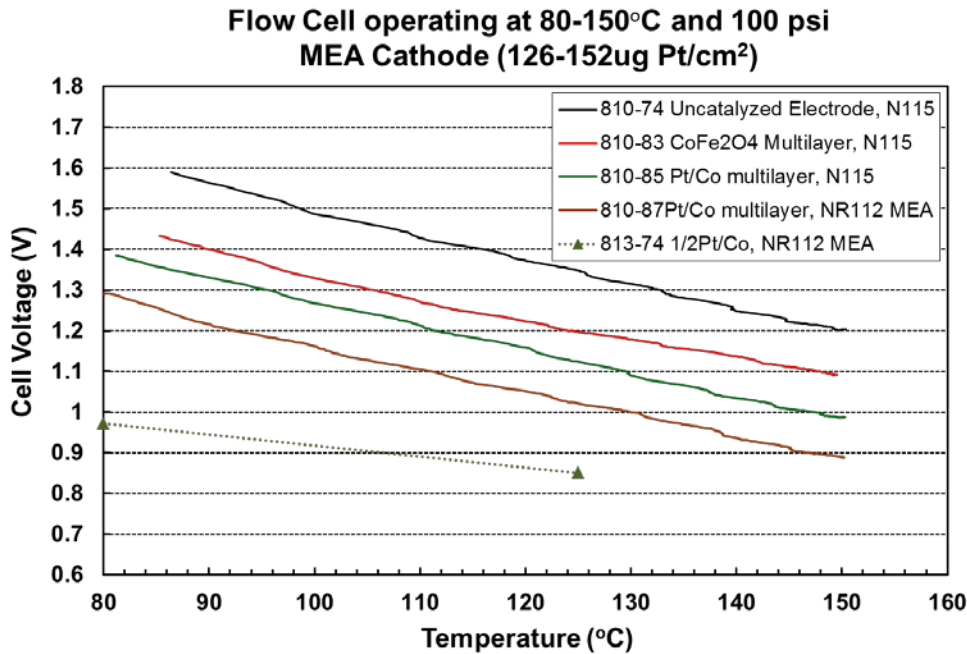
In acidic media

- anode reaction: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^o = 0.138$ V
- cathode reaction: $2H^+ + 2e^- \rightarrow H_2$ $E^o = 0.000$ V
- overall: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2 H^+ + H_2$ $E^o cell = -0.138$ V

In basic media

- anode reaction: $SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-$ $E^o = -0.936$ V
- cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^o = -0.828$ V
- overall: $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + H_2$ $E^o cell = 0.108$ V

Improvements in Electrocatalysis

Flow Cell operating at 80-150°C and 100 psi
MEA Cathode (126-152ug Pt/cm^2)

Cell Voltage (V) vs Temperature (°C)

Legend:
- 810-74 Uncatalyzed Electrode, N115
- 810-83 CoFe2O4 Multilayer, N115
- 810-85 Pt/Co multilayer, N115
- 810-87 Pt/Co multilayer, NR112 MEA
- 813-74 1/2Pt/Co, NR112 MEA

- All data shown is at 300 mA/cm^2.

- Improvements in operating cell voltage can be attained by improving the catalyst and reducing the membrane resistance.

- Improvements in cell design also eliminate some of the resistive losses in the cell.

Efficiency

- ## First Law efficiency

  $$\eta = -(\Delta H^o_{f[H_2O]} + E)/Q$$

- ## Second Law efficiency

  $$\eta = -(\Delta G^o_{f[H_2O]} + E)/Q$$

- ## DOE working definition

  $$\eta = -\Delta H^o_{f[H_2O(g)]}/(Q + E/\eta_e)$$

where

η = Plant efficiency

$\Delta H^o_{f[H_2O]}$ = enthalpy of formation of water in standard state = -hhv

$\Delta H^o_{f[H_2O(g)]}$ = enthalpy of formation of water vapor in ideal gas state = -lhv

$\Delta G^o_{f[H_2O]}$ = Gibbs energy of formation of water in standard state

Q = Total heat input to cycle

E = Total electrical input to process or if negative the electrical output of the process

η_e = Efficiency by which consumed electricity is produced

Note: The First Law efficiency is the efficiency calculated from a heat balance around the total plant. The Second Law efficiency is the efficiency that, for a reversible process would be given by Carnot's Equation. The DOE working definition was designed to estimate the relative ranking of a cycle before the complete plant design was complete.

Hydrogen Production System

- Thermochemical Plant Sized for 50MW Thermal Input; Solar Plant Gives 65% Capacity Factor
- Solar Input at ~800°C to Mid-Temperature Reactor
- Low-Temperature Reactor is Adiabatic (heat supplied by heat capacities of input materials)
- High-Temperature Reactor is Electrically Heated to 1200°C
- Process Energy Recovery Produces 8 MW of Electrical Output (gross), which supplies all process and system needs

Energetics of Hydrogen Production

- Hydrogen LHV = 33.3 kWh/kg
- Commercial Water Electrolysis Systems are ~65% Efficient (~50 kWh/kg hydrogen) to LHV
- Sulfur-Ammonia Process Uses Heat:
  - 154 kWh/kg Thermal Input
  - At 25% thermal-to-electric efficiency, this would be 38.5 kWh/kg